St. Anthony Falls Laboratory
University of Minnesota

Use of Compost to Biodegrade Sediments Contaminated with Polycyclic Aromatic Hydrocarbons

By
Scott Kyser, Raymond Hozalski, John Gulliver
University of Minnesota Stormwater Assessment Project

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Executive Summary

Recently, concentrations of polycyclic aromatic hydrocarbons (PAHs) that are above the Minnesota Pollution Control Agency's recommended limits have been detected in stormwater pond sediments. These ponds are designed to collect solids from stormwater runoff and periodically need to be dredged. The toxicity of the sediments due to high PAH concentration is a concern in their eventual disposal, and cost effective disposal methods for these contaminated sediments need to be established. Based on the concept that PAHs in contaminated soil can be biodegraded when mixed with compost, this project sought to evaluate the effectiveness of using compost to biodegrade PAHs in contaminated sediment. Two sets of bench-top experiments were performed, allowing for the simulation of the conditions in a compost pile that would favor biodegradation of PAHs bound to sediment. These experiments were able to effectively simulate the conditions of a compost pile with demonstrated composting. PAH biodegradation was not found to have occurred in most of the experiments despite significant microbial activity. While a complete data set is not yet available, it is becoming clear that these specific PAH contaminated sediments are not easily degraded using compost. Potential limitations in the ability of compost to degrade PAHs are explored and future research is suggested.

Introduction

Wet detention ponds are used to treat stormwater by settling and collecting suspended sediment. The amount of sediment a wet detention pond can accumulate in the Twin Cities metro area can range from 200 to 1450 kg/ha/year, dependent on pond trap efficiency and watershed sediment yield (Polta et al. 2006). The City of Plymouth, MN, for example, could accumulate 101,000 cubic feet of sediment per year in its over 700 wet detention ponds assuming a conservative load of 500 kg/ha/year and a trap efficiency of 80%. Since the City of Plymouth, MN represents only 0.4% of Minnesota's area, the total volume of sediments accumulated in Minnesota wet detention ponds would be substantially larger. Wet detention ponds in Minnesota are typically designed with a 25 year design life and the Minnesota Pollution Control Agency recommends that the ponds be dredged every 2 to 7 years (MPCA, 2009). Many of the wet detention ponds in Minnesota are reaching the end of their design life and have a sediment load that requires dredging to maintain performance.

The management of dredged material in Minnesota is subject to regulatory control and all sediment must be tested for pollutants prior to the initiation of any dredging activity. Sediments are typically tested for common parameters such as heavy metals, nitrogen, phosphorus, organic content and sieve size but based on the reasonable likelihood of their occurrence the sediments could be tested for other contaminants. The Minnesota Pollution Control Agency has developed dredged material soil reference

toxicity values that categorize sediment contaminants into different management tiers depending on their potential for toxicity. The three management tiers categorize sediments as either 1) safe for residential reuse 2) safe for industrial reuse 3) as having significant contamination that might require regulation under the Resource Conservation Recovery Act and/or the Toxic Substances Control Act.

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compound regulated under the MPCAs dredged material guidelines. They are products of incomplete combustion and have suspected or confirmed carcinogenicity (Larsen et. al., 2003, Hoffman et. al., 2009, Bouchard et al., 2009). While naturally occurring PAHs can accumulate in sediments (Achten C., 2009), the majority of PAH contaminated sediments worldwide can be traced to anthropogenic sources (Arp et. al, 2009). Anthropogenic sources of PAHs in sediments are typically associated with fossil fuel combustion and other industrial sources (Jiao et al., 2009). Recently, there has been an emerging trend relating urbanization to PAH concentration in sediments (Mahler et. al. 2005 & 2010, Cavalcante et. al, 2009).

Concern about PAH concentration in Minnesota wet detention pond sediments prompted the City of White Bear Lake to commission a study by Braun Intertec that showed that certain ponds in the White Bear Lake area had elevated levels of PAHs. A few ponds sediments exceeded the third tier of the states soil reference value toxicity guidelines for PAHs and could potentially require disposal in a confined disposal facility. The study also documented that PAH concentrations showed strong spatial variability both in terms of depth and location within a wet detention pond. While some these PAH concentrations are above the Minnesota third tier regulatory limit, the sediment

concentrations are approximately 4 to 225 times lower than PAH concentrations found in typical industrially contaminated sites such as creosote factories or a manufacturing gas plant (Antizar-Ladislao et. al. 2004).

Given the substantial volumes of wet detention pond sediments in Minnesota and the potential for a portion of these sediment to be contaminated with PAHs, various methods of PAH remediation have been considered. Bioremediation using compost was identified as a possible method to remediate PAH contaminated sediments. Various authors have found that by mixing compost with PAH contaminated soil or waste, naturally occurring organisms will degrade PAHs both at the bench scale (Hafidi et al. 2008, Carlstrom et al. 2003, Potter et al., 1999) and at the field scale (Cai. et al. 2007, Amir et al 2005). PAH concentrations typically exhibit a first order decay in a compost pile with smaller ringed PAHs being degraded faster than larger ringed PAHs. A small fraction (typically 4-21% of total PAH) cannot be degraded with this fraction being dominated by 4-6 ring PAHs (Antizar-Ladislao, 2005). Several key factors have been identified in using compost to bioremediate contaminated wastes such as maintaining aerobic conditions, ensuring adequate moisture, providing nutrients in the correct ratios and ensuring that the compost pile doesn't exceed temperatures that might inhibit microbial growth and diversity (Semple et al. 2001, Loick et al., 2009). Bioremediation with composting provides a number of benefits over other remediation methods because it can be accomplished at a large scale, uses local waste material and has the potential to be less expensive than other remediation methods.

While the bioremediation of PAH contaminated soils has been extensively documented, the composting of PAH contaminated sediment has not, to the authors

knowledge, been documented. The goal of this study is to evaluate the feasibility of using compost to biodegrade PAHs in the contaminated wet detention pond sediment from one pond in the City of White Bear Lake.

Methods

Sediment sampling

All sediments were sampled from the north end of pepper tree pond in White Bear Lake MN. Samples were collected with a MPCA sediment corer or a shovel from within a 5 meter area of the north stormwater inlet of the pond. Samples were collected from a sediment depth of 0 to 12 inches and stored in cleaned glass or Teflon containers and kept away from the sunlight. Approximately 20 liters of sediment were taken. All samples were homogenized before use and kept stored in a dark freezer.

Sediment Characterization

Moisture, ash content and pH were measured according to the Test Method for Evaluation of Compost and Composting. Sulfate and carbon content were analyzed at the University of Minnesota Soil Testing Laboratory (Soil Testing Laboratory, 2010).

PAH Quantification

Three to five grams of homogenized sample were Soxhlet extracted with dichloromethane for 24 hours. Samples were then condensed, passed through an alumina/silica cleanup column, transferred to hexane and condensed to approximately 1 ml. Five deuterated surrogate standards added were used to quantify procedural losses and five deuterated internal standards were used for PAH quantification. Samples with surrogate recoveries ranging between 70% and 120% were accepted as valid. A process blank was run with each sample run with surrogate recoveries ranging from 19-113%

with an average of 78%. Dibenzo(a,h)acridene and Dibenzo(a,j)acridene, Dibenzo(a,e)pyrene, Dibenzo(a,h)pyrene and Dibenzo(a,i)pyrene were quantified but were not identified as being distinct from each other. Further chromatographic tests are being completed to individually identify these compounds.

All samples were measured on a Hewlett-Packard 5890 series gas chromatograph with a series 5972 mass spectrometer and a 6890 series injector. Hewlett Packard MS Chemstation software was used to integrate peaks and operate the instrument. The injection port was operated in split mode with a 1:1 split ratio and a temperature of 280°C with helium as the carrier gas. The injection volume was 5 μL . Inlet pressure was varied by electronic pneumatic control to maintain a constant column flow of 1 ml min^{-1}. Compounds were separated on a Restek RTX®-XLB column (#800129, 30 m × 0.25 mm × 0.25 μm). The column was heated to 125°C at 25°C min^{-1} for five minutes, 8°C min^{-1} to 290°C for 17 minutes and then at 8°C min^{-1} to 310°C until 49 minutes. The mass spectrometer transfer line was maintained at 310°C.

Compost

The compost mixture was made of wood mulch, fallen leaves, fresh grass and was adjusted with urea to a carbon to nitrogen ratio of 30:1. The carbon to nitrogen ratio of each material was either determined by the Soil Testing Laboratory at the University of Minnesota or taken from Haug (1993). Compost from the city of Roseville, MN compost facility was used as a microbial innoculum.

Experimental Apparatus

Two experimental apparatuses were used. The constant temperature reactor (Figure 1) was adapted from that created by (Antizar-Ladislao, 2006). The variable temperature reactor (Figure 2) was adapted from that used by (Cook et al., 1994).

Constant temperature reactors

The temperature controlled reactors were maintained at a constant temperature of 38ºC to maintain mesophilic conditions. A total of 36 0.5 liter reactors were connected to an air distribution manifold shown in Figure 1. Humidified air was pumped into the bottom of each reactor and allowed to flow through the compost matrix, as illustrated in Figure 1. Flow was supplied at a rate of 1.3 m^3 day^{-1} kg^{-1} during for the first ten days and then was dropped to a rate of 0.7 m^3 day^{-1} kg^{-1} until the end of the experiment according to Cook et. al.(1994). Twelve reactors were used for each of the three amendments of 60%, 75%, 85% of sediment to compost by mass, for a total of 36 reactors. At sampling periods of 0,10,25 and 60 days, three reactors were sacrificed from each amendment and were stored in a freezer until analysis.

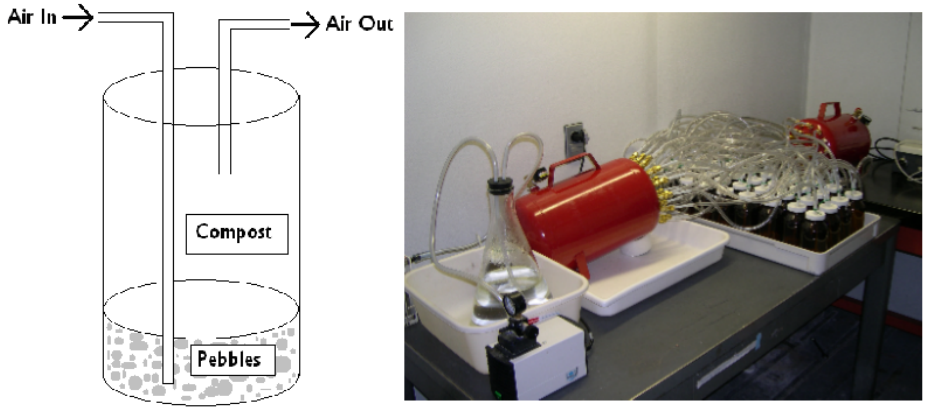

Figure 1. Schematic and photo of the temperature controlled reactor. The illustration shows a close up of the 0.5 L reactors. The photo shows the entire apparatus including the air humidifying step, the air distribution manifolds and the 36 reactors.

Variable temperature Reactor

The variable temperature reactor allows for a natural temperature progression and microbial diversity of the compost pile and a quantification of evolved carbon dioxide and volatilized PAHs. Compost temperature was allowed to progress naturally by a feedback system that minimized heat loss to the surroundings, mimicking the insulating capacity of a compost pile. The sediment was mixed with compost at 60%, 75% and 85% sediment to compost by dry mass and dispensed into one of the three reactors. Each reactor held a volume of 5 liters. The reactors were supplied with air in excess of the stoichiometric oxygen demand at a rate of 1.3 m^3 day^{-1} kg^{-1} during the self heating period and then flow was dropped to a rate of 0.7 m^3 day^{-1} kg^{-1} for the rest of the trial. The ash and moisture content was monitored at each sampling and moisture content was maintained at 50 percent. Compost samples were sampled from each reactor at 0, 10, 25, 60 and 90 days and stored in a freezer until analysis.

Figure 2. Schematic of one variable temperature reactor.

Evolved gases

Carbon dioxide was removed from influent air using a KOH scrubbing train. Carbon dioxide evolved from the compost piles was trapped in two KOH traps (Figure 2). The KOH for each reactor was changed and analyzed for carbon dioxide content at 0, 2, 4, 6, 8, 11, 24, 29, 42, 57 and 90 days. Carbon dioxide content in solution was measured by precipitating carbon dioxide using excess barium chloride and then titrating to the phenolphthalein red end point with 1M HCl (Methods of Soil Analysis-Part 2, 1982). Volatilized PAHs were trapped using orbo-43 tubes that were replaced every time the KOH solutions were sampled.

Results

As of this writing not all samples have been analyzed. Samples that have and have not been analyzed are available in Table 1 and Table 2.

		60% Sediment			75% Sediment			85% Sediment	
Reactor number	#1	#2	#3	#1	#2	#3	#1	#2	#3
Day 0	x	x	x	x	x	x	x	x	x
Day 10									
Day 25									
Day 60									
Day 90	x								x

Table 1. Samples processed for the constant temperature reactors as of the writing of this report. X indicates that the samples have been satisfactorily analyzed.

	60% Sediment	75% Sediment	85% Sediment
Day 0	x	x	x
Day 10	x		
Day 25	x		
Day 60			
Day 90	x		x

Table 2. Samples processed for the variable temperature reactors as of the writing of this report. X indicates that the samples have been satisfactorily analyzed.

Sediment Characterization

The concentration of PAHs in the sediment taken from the north side of Pepper tree pond in White Bear Lake, MN are given in Figure 3. The dessicated sediment had a volatile solids content of 98%, an organic content of 0.5%, and a sulfate content of 30 ppm. Detectable PAH concentrations ranged from 0 to 16.25 mg/kg dry weight. The total PAH level was 90.09 mg/kg-dry weight with 91.2% of the PAHs having four or more rings. Methylated PAHs comprised 0.9% of the total detected PAH levels. According to the MPCA soil reference values the sediment had the equivalent toxicity of 15.6 mg Benzo[A]Pyrene /kg-dry weight, placing it in the tier III category that might require disposal in a hazardous waste landfill.

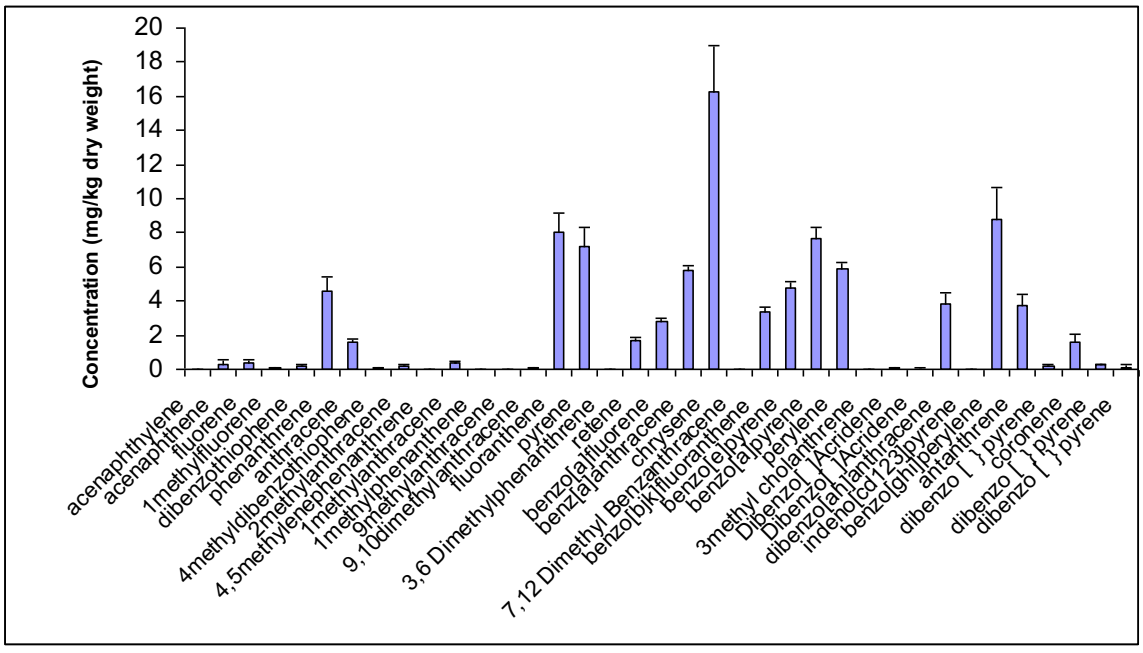

Figure 3. Concentration of PAHs in the sediment taken from the north side of Pepper tree pond in White Bear Lake, MN. The error bars represent the standard deviation among three replicate samples.

Temperature Controlled Reactors

The temperature controlled reactors showed variable PAH degradation. The 85 percent sediment to compost reactor showed a decrease in PAH concentration (Figure 4). Three and four ring PAHs such as phenanthrene, anthracene, fluoranthene and pyrene all showed over 60% degradation. Five and six ring PAHs also exhibited degradation but less than three or four ring PAHs.

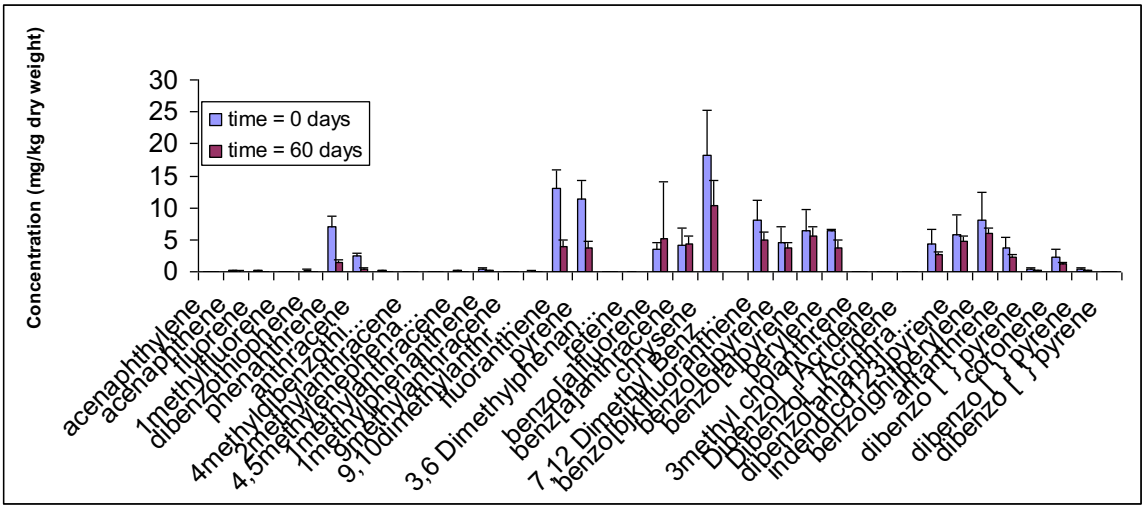

Figure 4. Temperature controlled reactor 85% sediment to compost. The error bars represent the standard deviation among triplicate samples.

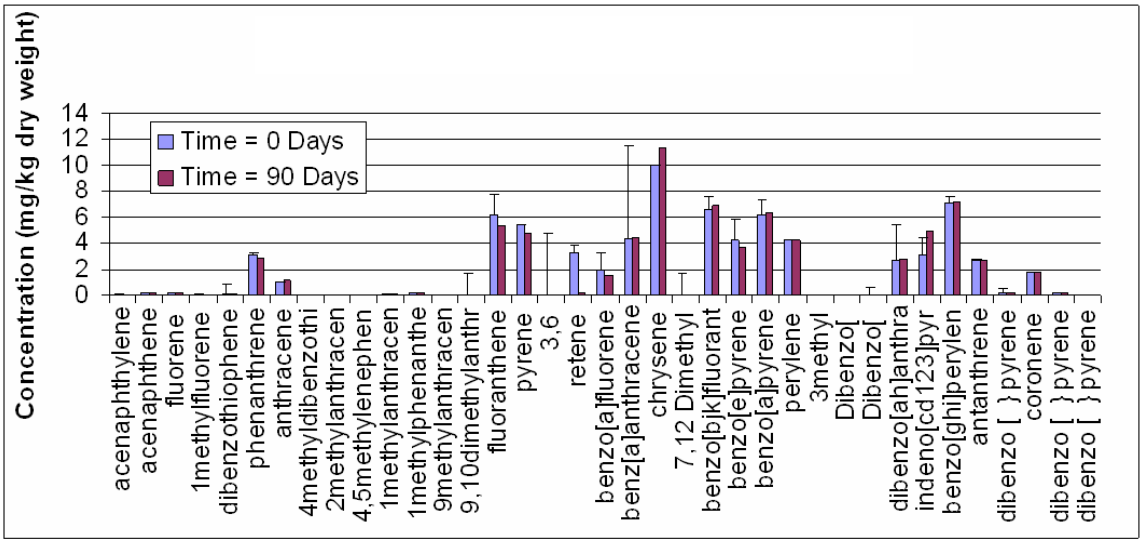

Figure 5. Temperature controlled reactor 75% sediment to compost. The error bars represent the standard deviation among triplicate samples.

The 75% sediment to compost temperature controlled reactors did not have significant degradation (Figure 5). The 60% sediment reactors were not included in this report because of excessive surrogate losses and lost peaks during initial analysis.

Variable Temperature Reactors

The temperature of a compost pile can be used as an indicator of microbial activity with higher temperatures correlating to higher microbial activity (Haug, 1993). All of the reactors exhibited an increase in temperature above baseline for a period of ten days and then stayed at 25ºC for the remainder of the trial (Figure 6). The reactor with the greatest ratio of compost to sediment self-heated to a maximum temperature of 40ºC and the reactor with smallest ratio of compost to sediment self-heated to a maximum temperature of 29ºC. The 60% sediment reactor was the only reactor to enter the high mesophilic (35ºC - 40ºC) temperature range which is the range at which PAH degrading microbes have been shown to be most effective (Antizar-Ladislao, 2005).

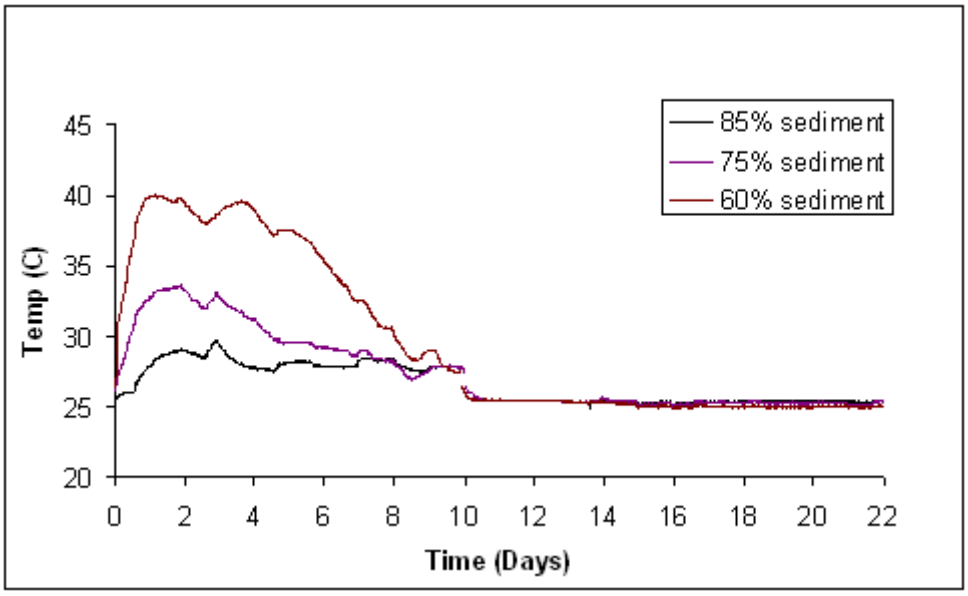

Figure 6. Temperature profile of the variable temperature reactors. The broken line at ten days represents the time when the reactors were sampled.

Carbon Dioxide Evolution

Over the course of the trial all reactors evolved more than 40% of their initial carbon content as carbon dioxide (Figure 7). The three reactors evolved more than half of their total carbon loss during the first ten days with the reactor with the highest ratio of compost evolving the greatest percent of initial carbon. The amount of carbon evolved from a compost pile is proportional to total microbial activity (Cook et al, 1997). The high carbon loss from each pile can be seen as an indicator of substantial microbial activity in all of the piles, particularly during the first ten days of composting.

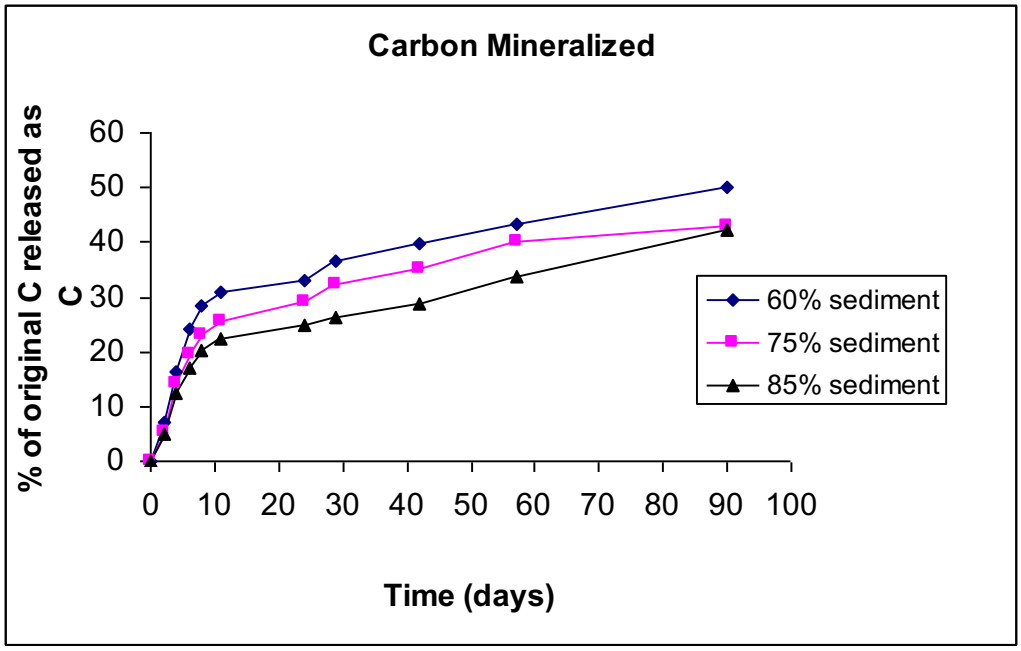

Figure 7. Cumulative evolved carbon dioxide from the variable temperature reactors normalized to the initial carbon content present in the reactor.

Ash Content

Ash content as a percent of the total dry mass increased for both the 85% sediment reactors (t-test, n=6, p=0.008) and the 75% sediment reactors (t-test, n=6, p=0.005) over the course of the trial. The 60% sediment reactor did not show a significant ash content change from 0 to 90 days, but the test is complicated by large standard deviation attributable to heterogeneity in the compost matrix (Figure 8). The ash mass of a compost matrix is inorganic, non-volatile and not available to organisms and is thus fixed over time. The increase in percent ash content indicates that mass was lost from the piles in the form of volatilized or mineralized organic matter which is another indicator of microbial activity.

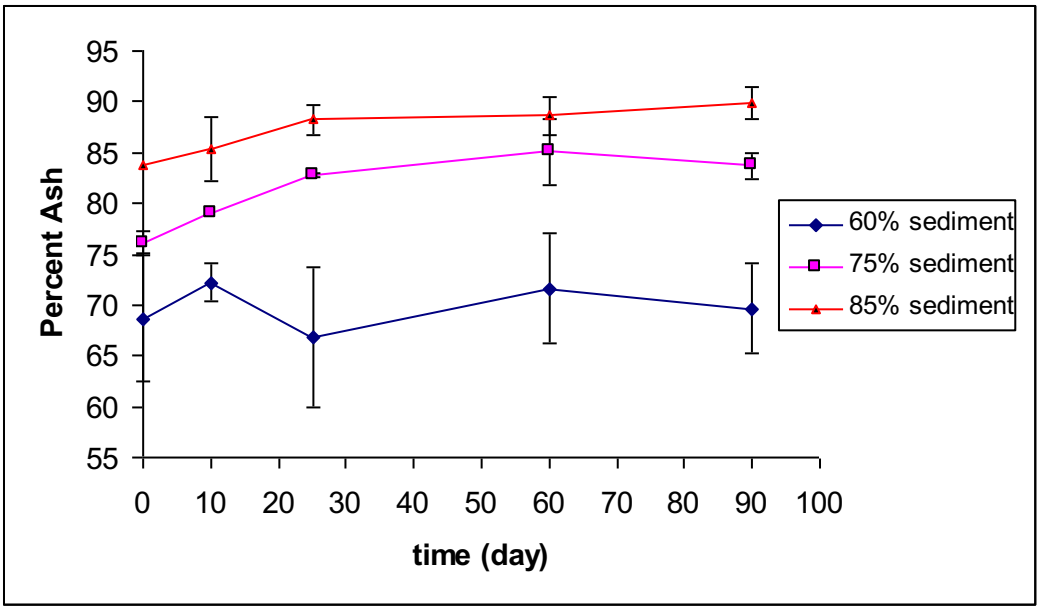

Figure 8. Percent ash content of the variable temperature reactors over the course of the trial.

PAH Levels during composting

PAH concentrations did not decrease for the 60% sediment reactor over the course of treatment, (Figure 9). The 75% sediment reactor was not included in this report because of excessive surrogate losses and lost peaks during initial analysis. PAH levels increased for the 85% sediment reactor (Figure 10) as the total dry weight of the reactor decreased. Smaller ring PAHs were not preferentially degraded over larger ring PAHs. It is unlikely that PAH losses due to volatilization occurred in the reactors because no change in PAH concentration was observed.

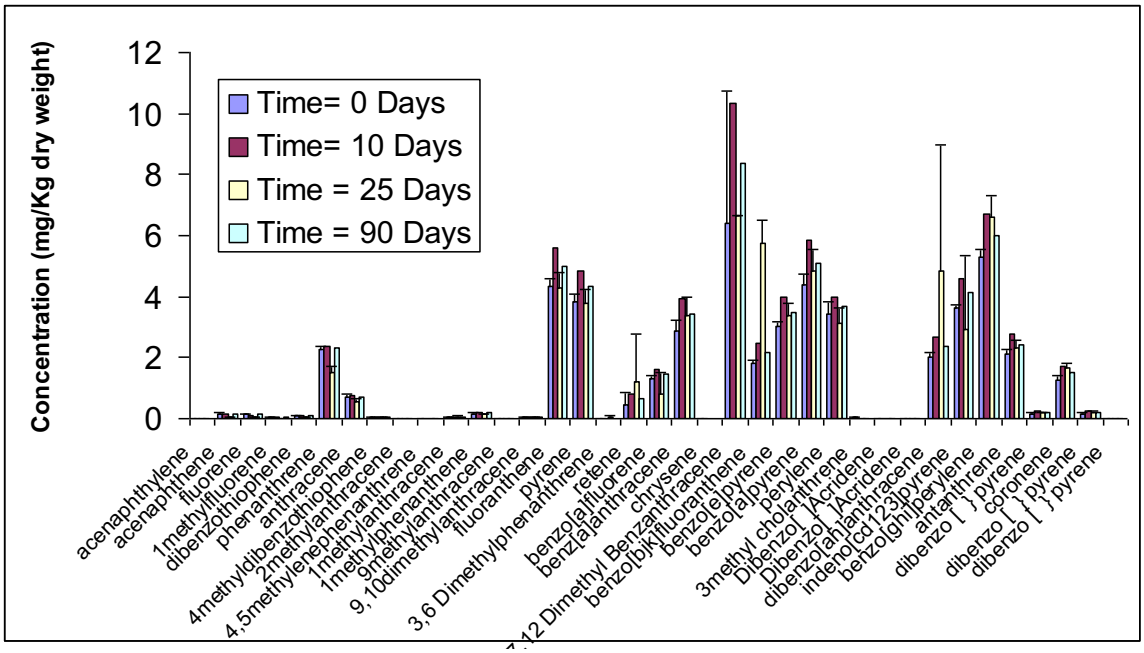

Figure 9. PAH concentrations of the 60% sediment to compost reactor at 0,10,25 and 90 days. The error bars represent standard deviation among three replicate samples, if no error bars are present the sample was not run in triplicate.

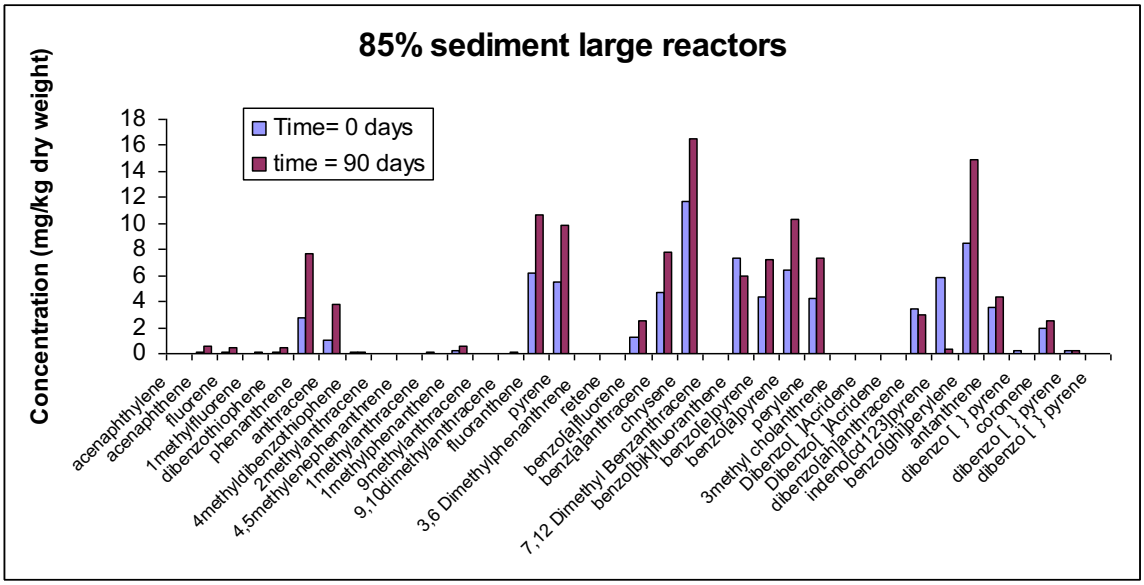

Figure 10. PAH concentration of the 85% sediment to compost variable temperature reactor from 0 to 90 days.

The large error bars and increase in PAH concentration in figures 9 and 10 illustrate the difficulties in getting a representative sample of PAHs in a compost matrix . A subsample of 3-5 grams of compost may not always be representative of the larger

compost pile due to the small scale heterogeneity of a compost pile. It has also been reported that measured PAH concentrations can increase during composting of soils likely due to mineralization of volatile solids that increase the ratio of PAH mass to compost mass even though absolute PAH mass loss was observed (Antizar-Ladislao, 2005).

Discussion

Variable Temperature Reactors

PAH levels in the variable temperature reactors did not decrease over 90 days of composting trial even though there was strong evidence of microbial activity. The increase in temperature of the reactors, the evolution of mineralized carbon dioxide and the increase in ash content over time all indicate that substantial microbial activity took place. There are two possible explanations for why the biodegradation of PAHs did not occur:

1) It is possible that PAH degrading microbes were not present in the compost matrix. This is unlikely because authors have found endogenous PAH degrading microbes in compost in diverse locations such as Morrocco (Hafidi et. al, 2008), Finland (Haapea et. al., 2006) and Hong Kong (Lau et. al., 2003). The potential for microorganisms in soil to biodegrade PAH has been correlated with the presence of low levels of four ring PAHs in the soil and urbanization (Johnsen and Karlson, 2005). Since low levels of four ring PAHs such as pyrene and chrysene were detected in the pure compost (Appendix, Table A2), it is reasonable to assume that organisms expressing PAH degrading genes were present in the compost. The use of microbial techniques to identify PAH

degrading microbes could be used to retroactively confirm the presence of PAH degraders .

2) It is possible that the PAHs were bound strongly to the sediment and not available for microbes to degrade. There has been a wealth of research over the past fifteen years showing that the total concentration of PAHs on sediment are not representative of fraction of PAHs that are available to organisms. Current theory suggests that only compounds that are soluble in water are available to organisms. The water soluble portion of PAHs partitioned from sediments is not well predicted with traditional methods such as using the total PAH content, sorption to the fraction of organic carbon, the octanol to water partitioning coefficient or Biota to Sediment Accumulation Factors . The current best predictor of PAH bioavailability to organisms from sediments is the pore water fraction or the portion of PAHs from sediments that partition into water (Arp et. al, 2010, Ghosh et al. 2010, Ehlers et al. 2003). The pore-water fraction can be used to predict the extent of biodegradation of PAHs on sediment and soils (Lei et. al. 2004, Ahn et. al., 2005). The pore-water fraction of PAHs can also be used to predict the toxicity of PAHs in a sediment matrix (Kreitinger et. al 2007, Hawthorne et. al., 2007).

Conclusion

Wet detention pond sediments contaminated with PAH compounds were not reliably degraded using compost remediation. The majority of samples in the variable temperature reactors did not show any significant degradation with some reactors showing an increase in PAH concentration despite substantial evidence of microbial

activity. The constant temperature reactors exhibited variable PAH degradation with one reactor showing no change in PAH concentrations and one reactor showing a decrease in PAH concentration. The lack of degradation of many of these samples may be limited by availability of PAHs to degrading organisms. Determination of the bioavailable fraction of PAHs from the sediment is a suggested next step, because it may have implications for PAH remediation and toxicity guidelines.

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Appendix 1

Table A1. Pure Sediment PAH Concentrations in Pepper Tree Pond, White Bear Lake, MN

Compound Name	Concentration (mg/kg-dry weight)	Standard Deviation
acenaphthylene	0.02	0.01
acenaphthene	0.32	0.20
fluorene	0.42	0.10
1methylfluorene	0.09	0.01
dibenzothiophene	0.21	0.04
phenanthrene	4.59	0.83
anthracene	1.60	0.19
4methyldibenzothiophene	0.07	0.00
2methylanthracene	0.17	0.15
4,5methylenephenanthrene	0.00	0.00
1methylanthracene	0.42	0.01
1methylphenanthene	0.01	0.00
9methylanthracene	0.00	0.00
9,10dimethylanthracene	0.06	0.01
fluoranthene	8.01	1.14
pyrene	7.21	1.09
3,6 Dimethylphenanthrene	0.00	0.00
retene	1.67	0.16
benzo[a]fluorene	2.78	0.22
benz[a]anthracene	5.77	0.34
chrysene	16.25	2.75
7,12 Dimethyl Benzanthracene	0.01	0.00
benzo[bjk]fluoranthene	3.38	0.31
benzo[e]pyrene	4.80	0.31
benzo[a]pyrene	7.69	0.58
perylene	5.90	0.35
3methyl cholanthrene	0.00	0.00
Dibenzo[ ]Acridene	0.07	0.02
Dibenzo[ ]Acridene	0.04	0.04
dibenzo[ah]anthracene	3.82	0.62
indeno[cd123]pyrene	0.00	0.00
benzo[ghi]perylene	8.78	1.87
antanthrene	3.75	0.61
dibenzo [ ] pyrene	0.22	0.06
coronene	1.59	0.47
dibenzo [ ] pyrene	0.24	0.08
dibenzo [ ] pyrene	0.14	0.17

Table A2. Pure Compost PAH concentrations

Compound Name	Concentration (mg/kg-dry weight)
acenaphthylene	0.00
acenaphthene	0.02
fluorene	0.00
1methylfluorene	0.00
dibenzothiophene	0.00
phenanthrene	0.09
anthracene	0.02
4methyldibenzothiophene	0.00
2methylanthracene	0.00
4,5methylenephenanthrene	0.00
1methylanthracene	0.02
1methylphenanthene	0.00
9methylanthracene	0.00
9,10dimethylanthracene	0.00
fluoranthene	0.17
pyrene	0.15
3,6 Dimethylphenanthrene	0.00
retene	0.00
benzo[a]fluorene	0.06
benz[a]anthracene	0.10
chrysene	0.37
7,12 Dimethyl Benzanthracene	0.02
benzo[bjk]fluoranthene	0.13
benzo[e]pyrene	0.00
benzo[a]pyrene	0.00
perylene	0.00
3methyl cholanthrene	0.00
Dibenzo[ ]Acridene	0.00
Dibenzo[ ]Acridene	0.00
dibenzo[ah]anthracene	0.30
indeno[cd123]pyrene	0.16
benzo[ghi]perylene	0.00
antanthrene	0.00
dibenzo [} pyrene	0.00
coronene	0.00
dibenzo [} pyrene	0.00
dibenzo [} pyrene	0.00

Appendix 2. PAH sediment to water partitioning.

This appendix documents the progress of additional preliminary research that is supported by the University of Minnesota. It is relevant to the portion of the PAHs on sediments that is refractory, or water soluble. It is believed that the compounds must be water soluble to be biologically available, except to specialized bacteria not generally available in pond sediments.

Introduction

The portion of PAHs that partitioned into water from the sediment was determined using a XAD-2 water extraction procedure similar to that of Lei et. al.(2004). The XAD-2 acts as an infinite sink for PAHs causing a concentration gradient that de-sorbs PAHs from the sediment into the water and onto the XAD-2 (Figure A3). By measuring the portion of PAHs that partitioned to the XAD-2 from the sediment over time an understanding of PAH sediment-water partitioning and presumed PAH bioavailability can be gained.

Methods

1.4 g of sediment was added to 25 ml of pH 6.5 buffered water in a glass centrifuge tube and the 2.8 g XAD-2 was added and allowed to float on the top of the water column (Figure 1). The centrifuge tube was then put onto a manual shaker and the XAD-2 was sampled at 24 and 48 hours, further experiments analyzing desorption at 14 and 21 days have yet to be analyzed. The XAD-2 was sonicated in dichloromethane three times to desorb PAHs sorbed on the XAD-2. The extract was then passed through a sodium sulfate column to remove excess water, rotovapped and analyzed on a GC/MS.

Figure A3. Illustration of the system used to monitor PAH desorption from sediment onto XAD-2. The fraction of PAHs originally present on the sediment that have partitioned onto the XAD-2 can be considered the fraction of PAHs that are soluble.

Results and Discussion

The fraction of PAHs that desorbed from the sediment into water and onto the sediment was low, ranging from 0 to 12 percent (Figure A4). In general, the more benzene rings the PAH had, the less likely it was to partition from the sediment into the water. Data at 24 and 28 hours is only shown for this experiment and shows some inconsistencies such as the detection of Dibenzo(a,h)Anthracene at 24 hours but not at 48 hours. Further data showing the mass of PAHs partitioned onto the XAD-2 at 14 and 21 days will give an understanding of PAH sediment desorption kinetics and the fraction of PAHs on the sediment that will not partition into the water and become bioavailable.

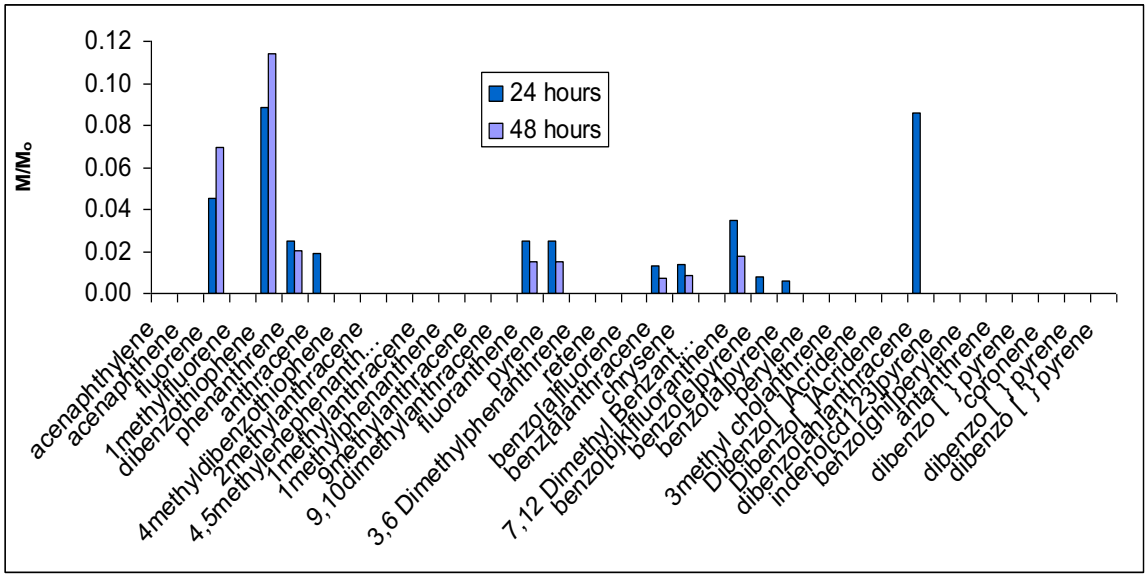

Figure A4. Mass of PAHs present on XAD-2 divided by the mass of PAHs originally present on the sediment at 24 and 48 hours. The mass of PAHs on the XAD-2 can be considered the mass of PAHs that partitioned into the water phase from the sediment. M is the mass of PAHs on the sediment. M_0 is the mass of PAHs originally on the sediment.

While this data is not complete it does strongly suggest that a significant portion of the PAHs on the sediment are not available to be partitioned into the water and become available to organisms. This is one explanation as to why little PAH degradation was noted in the PAH biodegradation experiments.

If the concentrations of PAHs that partitioned into the water after 24 hours is used to calculate the toxicity of the sediment, the toxicity drops from 15.6 mg Benzo[a]pyrene equivalents/kg-dry weight to 0.05 mg Benzo[a]pyrene equivalents/kg-dry weight, putting the sediment well within the tier I dredged materials safe for all uses classification. This indicates that total PAH levels in sediment may not be useful as a predictor of potential PAH toxicity.